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UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES  
PREPARATION OF NITROCOMPOUNDS. (U)  
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Nitration of aromatics was studied with mixed "fluoroacid" (i.e., $\text{FSO}_3\text{H}-\text{HWO}_3$ ), with transfer nitrating agent, such as N-nitropyrazole- $\text{BF}_3$ , and with $\text{Hg}^{++}$ impregnated Nafion-H catalyzed nitric acid under azeotropic water removal conditions. Both preparative and mechanistic aspects were investigated.		

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### Preparation of Nitrocompounds

Final Research Report: November 1, 1980 - October 31, 1981

A new preparative nitration method using mixed "fluoroacid,"  $\text{FSO}_3\text{H}$ - $\text{HNO}_3$  was developed, for the nitration of benzene to trinitrobenzene (TNB), of toluene to trinitrotoluene (TNT), as well as related polynitration of homologous alkylbenzenes. The system was also studied in conjunction with  $\text{BF}_3$  as a dehydrating agent. Eliminating the use of anhydrous  $\text{HF}$  and replacing it with easy to handle  $\text{FSO}_3\text{H}$  is of real preparative advantage. The system is superior to mixed acid ( $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$ ) and  $\text{HNO}_3$ -oleum systems, as the latter are also strong oxidizing agents and lead particularly under forcing polynitration conditions, to oxidative degradations.

Covalent new mixed anhydrides of nitric acid with trifluoromethanesulfonic acid and fluorosulfonic acid were studied as nitrating agents, and found effective in aromatic nitrations.

Two new nitrating agents, N-nitropyrazole/ $\text{BF}_3$  and  $\text{AgNO}_3/\text{BF}_3$  were developed and studied in aromatic nitration.

N-nitropyrazole in the presence of Lewis or Bronstead acid catalysts was found to be an effective transfer nitrating agent for aromatic substrates. The nature of the acid catalyst affects both substrate and positional selectivities of the nitration of alkylbenzenes. No relationship was found between substrate and positional selectivities, which are considered to be determined in two separate steps.

Transfer nitrations were also studied with N-nitroimidazole and pyrazole, and nitratotrimethoxyphosphonium salts. These new reagents give improved selectivities in transfer nitration reactions.

The use of pyridinium polyhydrogen fluoride as solvent medium for nitronium salt nitration of aromatics was found to be a substantially improved new nitration medium.

Benzene, alkylbenzenes, halobenzenes and anisole were nitrated with silver nitrate/boron trifluoride in acetonitrile solution. Correlation of competitive rates with  $\pi$  and  $\sigma$ -complex stabilities indicated that the transition state of highest energy lies relatively early on the reaction coordinate. Data indicate that nitrations occur via a polarized complex of the nitrating agent with the catalyst undergoing nucleophilic displacement by the aromatic substrate.

Alkylbenzenes, halobenzenes and naphthalene were nitrated with nitric acid under azeotropic conditions of removal of water with  $\text{Hg}^{++}$  impregnated Nafion-H perfluorinated sulfonic acid resin catalyst. The isomer ratios of nitroalkylbenzenes showed differences from conventional acid catalyzed nitrations yielding larger amounts of the less hindered isomer.

Naphthalene was nitrated with a variety of nitrating agents. Comparison of data with Perrin's electrochemical nitration shows that nitration of naphthalene gives an  $\alpha$ - to  $\beta$ -nitronaphthalene ratio varying from 9 to 29 and is thus not constant. Perrin's data, therefore, are considered inconclusive evidence for the proposed one electron transfer mechanism for nitration of naphthalene and other reactive aromatics.

Moodie and Schoefield, as well as Perrin, independently concluded that in the general scheme of nitration of reactive aromatics, there is the necessity to introduce into the classical Ingold mechanism, an additional step involving a distinct intermediate preceding the formation of the Wheland-intermediate ( $\sigma$ -complexes). This view coincides with our two-step mechanistic picture first suggested in 1961, of the nitronium salt nitration of aromatic hydrocarbons (including benzene and toluene) where low substrate but high positional selectivity was found, indicating the independence of substrate from positional selectivity.

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